

PATENT APPLICATION

Title: Chemical Synthesis Comprising Heat Treatment by Intermittent Dielectric Heating, Combined with a Recycling System

Inventor: Mr. Pierre Charlier de Chily
Mrs. Mikaële Raynard

Applicants: ALDIVIA S.A.

ABSTRACT

This invention relates to the design of a process by intermittent dielectric heating combined with a recycling system.

This process consists in subjecting reagents to electromagnetic waves selected in the frequencies ranging between 300 GHz and 3 MHz intermittently using a recycling system.

This process enables the treatment of oils that are hardly absorbent as well as great investment savings.

This process enables operation on different scales, whether in laboratories, on a semi-industrial or industrial scale, without forfeiting the advantages of continuous dielectric heating.

FIG. 1

**Chemical Synthesis Comprising Heat Treatment by
Intermittent Dielectric Heating, Combined with
a Recycling System**

Background of the Invention:

Regardless of the complexity of the molecule to be manufactured, chemists always try to find a way to reduce the reaction time and the number of steps required for synthesizing a molecule because of a constant concern regarding costs and profitability.

Many studies have been conducted for the purpose of controlling the various parameters capable of influencing the unfolding and speed of a reaction. Additives, such as solvents, catalysts, have been widely used. Although these compounds stimulate the reaction medium, they are sometimes toxic to man and the environment, and they require expensive post-treatments such as neutralization, washing, drying, filtration.

Today, the trend is toward manufacturing processes that are simple, low in cost, and respectful of man and his environment.

Some physical processes have been tested: the use of ultrasounds, high frequencies, and recently, microwaves.

The various tests conducted using dielectric heating, that is to say, heating under microwave frequencies or high frequencies, have shown the potential value of this new technology: indeed, dielectric heating permits considerable time and energy savings, combined with lower investment costs; the reactions no longer require the use of any solvent or catalyst; burn-up and unwanted reactions are avoided.

Although today there are available many types of high-frequency and microwave applicators, they are all nonetheless configured in such a way that the reaction medium is continuously exposed to electromagnetic waves in order to be able to benefit from the advantages inherent in this new technology. The amount of material processed in this

manner is limited, because it depends on the dimensions of the waveguides that are themselves standardized.

Summary of the Invention:

The applicant has discovered a new heat treatment process involved in a chemical synthesis: namely, intermittent dielectric heating combined with a recycling system. The reagents are subjected to electromagnetic waves on an intermittent basis using a recycling system. The electromagnetic waves are selected among the frequencies ranging from 300 GHz to 3 MHz.

This process is original and low in cost. Additionally, this process enables operation on different scales, whether in laboratories, on a semi-industrial or industrial scale, without forfeiting the advantages of continuous dielectric heating.

Applications:

The invention makes it possible to carry out efficient and rapid heat treatments on different scales, whether in laboratories, on a semi-industrial or on industrial scale.

This invention relates to all "heat applications," that is to say, the chemical syntheses involving a heat treatment and featuring a sole reagent, or a mixture of reagents, in variable proportions, with or without catalysts, with or without process gas.

As "heat applications," we can cite, as non-limitative examples, such reactions as esterification, transesterification, epoxydation, sulphatation, phosphitation, hydrogenation, peroxydation, isomerization, dehydration, quaternization, amidation, polymerization, polycondensation, and all the common treatments such as decolorizing, deodorizing, and the other systems for eliminating volatile compounds.

The invention in fact applies very specifically to all "lipochemistry" reactions.

This innovative technique permits, for example, manufacturing polymers of unsaturated fatty acids, esters of unsaturated fatty acids, unsaturated hydrocarbons or derivatives of these products using intermittent dielectric heating under microwaves. In this connection, the applicant has filed a Patent Application FR 98 13770 and a Patent Application PCT WO 00/ 26265 (PCT / FR 99 / 02646).

Prior Art:

The field of this invention relates to the use of microwave (MW) or high frequency (HF) electromagnetic waves for any heat treatment.

- The MW and HF frequencies

The MW microwave frequencies are comprised between about 300 MHz and about 30 GHz, preferably at 915 MHz (authorized frequency with a tolerance of 1.4%) or at 2.45 GHz (authorized frequency with a tolerance of 2%).

The HF high frequencies are comprised between about 3 MHz and about 300 MHz, preferably at 13.56 MHz (authorized frequency with a tolerance of 0.05%) or at 27.12 MHz (authorized frequency with a tolerance of 0.6%).

- Absorbed Power

The Absorbed Power (AP) is a dependent variable of the Incident Power (IP) and of system losses.

For a product that hardly absorbs electromagnetic waves, and for a given Incident Power (IP), the Absorbed Power (AP) decreases and the losses increase, in particular those losses due to static electricity.

Indeed:

$$\mathbf{IP = AP + losses}$$

Wherein:

IP = Incident Power in Watts

AP = Absorbed Power in Watts

Losses = heat losses + static electricity

The Absorbed Power (in Watts) by a material under HF or MW treatment is expressed by the following formula:

$$\mathbf{AP = kf \epsilon'' E^2 V}$$

with:

AP : Absorbed Power in Watts

E : electric field created inside the material in V/cm

f : frequency of wave

K : constant (M.K.S.A) = $5.56.10^{-13}$

V : volume of material in cm^3

ϵ'' : material loss factor = $\epsilon' \tan \delta$

ϵ' : actual relative permittivity of the material = $\epsilon_0^* \epsilon_r$

$\epsilon \epsilon_0$: permittivity of vacuum

ϵ_R : dielectric constant

$\tan \delta$: angle of losses

ϵ' translates the ability of a material to orient itself in the field, and $\tan \delta$ its ability to release heat.

Note: For air or vacuum, $\epsilon' = 1$ (lowest value for ϵ') and $\tan \delta = 0$, i.e., $\epsilon'' = 0$.

- type of energy applicators

The type of energy applicator selected depends on the technology used (high frequencies or microwaves), the dimensional characteristics of the product to be treated and its mode of treatment.

As regards high frequency applicators, these essentially consist in:

- applicators of the capacitive type formed by two condenser armatures between which the generator's high-frequency voltage is applied. They are used for the heat treatment of materials whose volume constitutes a parallelepiped, one side of which is sufficiently thick (>10 mm).
- applicators with rods for planar materials. These applicators are made up of tubular or rod-shaped electrodes. They are used for the heat treatment of materials whose volume constitutes a parallelepiped, one side of which is insufficiently thick (<10 mm).
- applicators for filiform materials, formed by loops.

For the microwave applicators, we can cite:

- localized-field applicators: singlemode cavity
- diffuse-field applicators: multimode cavity
- near-field applicators: {wave}guide with radiating antennas

Among these microwave applicators, there are available on the market for example:

- the "synthewave 402" and the "synthewave 1000" that are made up of 1ml to 100ml or 600ml reactors
- the "Discover" with 1ml to 125ml reactors
- the "Ethos MR" with a capacity of less than 400 ml
- *risks of electrical breakdown or electric arcs*

The Applicant has filed a Patent Application FR N° 0108906 concerning an improved apparatus for carrying out dielectric heating. In said patent, the invention relates to a new shape or geometry of a chimney, in particular a chimney with a conical shape or geometry, which permits heating any type of product under microwave frequencies or high frequencies, in statics or dynamics with a sizeable power density without any risk of electric arcs or electrical breakdown.

Any person skilled in the art may refer to said patent application for further details. For his/her convenience, a summary thereof is provided hereinbelow.

- In the case of hardly absorbent molecules, the choice of applicators is complicated. The applicator in fact has to transmit a great deal of electromagnetic energy to the product in order to be able to provide heat while avoiding electric arcs.
- Heating under microwave frequencies is preferable to heating under high frequencies for which the risk of electrical breakdown is greater.
- The "singlemode" system (localized field) which is formed by singlemode cavities resonating at the transmission frequency according to a radiation in the direction of the [wave]guide is preferred to the "multimode" (diffuse field). The singlemode system avoids a non-homogeneous distribution of the electric field and the presence of hot points. Likewise, this type of reactor creates stability in the products exposed.
- The singlemode applicator outfitted with the usual cylindrical chimneys, which is the most suitable one of all common applicators with hardly absorbent molecules, does not permit working with a high density of power without running the risk of electrical breakdown.
- Nonetheless, the introducing into the reaction medium of some polar compounds such as water, so as to play the role of intermediary in energy transfer and thus reduce the density of power needed, is still not satisfactory. Unwanted side reactions can take place, making supplemental treatments such as neutralization, washing, drying or filtration necessary to purify the product at the end of the reaction.
- One alternative to mitigate the problems related to the hardly absorbent compounds is to eliminate the static electricity as it forms on the outer wall of the reactor. In order to eliminate the static electricity, one must either make for a good ventilation using humid air or some other gas that is comparable from the standpoint of its

dielectric constants (for example: sulfur hexafluoride SF6 under 1 bar) (1st solution), or adapt the shapes of the chimneys so as to aerate them (2nd solution). The first solution is not attractive due to the complexity of equipment, safety issues, and cost reasons.

- The applicant has discovered a new chimney shape or geometry, in particular a conical chimney, that makes it possible to heat any type of products under microwave frequencies or high frequencies, in statics or in dynamics, with a sizeable power density without any risk of electric arcs or electrical breakdown.

Description of the Invention:

The applicant has discovered a new heat treatment process that consists of submitting the reagent, either alone or in a mixture, to electromagnetic waves in an intermittent manner, with the help of a recycling system.

The electromagnetic waves are selected in the frequencies ranging between 300 GHz and 3 MHz.

This process retains the advantages of continuous dielectric heating while increasing production capacity.

- Description of the Equipment

The intermittent heating process is simple and low-cost. It consists of :

- pumps

- reactors subjected to the electromagnetic field
- a dielectric system: chimney applicators, generator waveguides, iris, shortcircuit piston, cooling systems
- buffer reactors
- tanks
- a gas circuit, preferably for an inert gas such as nitrogen
- condensers
- measuring devices

The Pumps

The pump(s) is (are) of the variable-flow type.

It can be a feeder dosing pump and/or a recycling pump and/or a vacuum pump. The outflow of the recycling pump influences the time required for a molecule to transit under the waves.

The pumps can be selected, for purposes of indication, from among vane pumps or piston pumps.

Reactors subjected to the Electromagnetic Field

The reactors subjected to the electromagnetic field do not absorb the waves (pyrex, quartz, etc.).

They are typically cylindrical in shape.

They are positioned inside applicators.

Dielectric system: chimney applicators, generator waveguides, iris, shortcircuit piston, cooling systems

The applicators are formed by singlemode cavities that resonate at the transmission frequency according to a radiation in the direction of the waveguide.

The chimneys prevent wave leakage to the outside of the waveguide. They are preferably of a conical cylindrical shape, as indicated in Application FR N° 0108906 filed by this Applicant for limiting the presence of electric arcs.

The waveguide(s) carries/carry the electromagnetic waves. Each waveguide can be subdivided into two — and only two — waveguides.

The generators used are microwave or high-frequency generators.

The microwave (MW) frequencies range from about 300 MHz to about 30 GHz, preferably standing at 915 MHz (authorized frequency with a tolerance of 1.4%) or at 2.45 GHz (authorized frequency with a tolerance of 2%).

The high frequencies (HF) range from about 3 MHz to about 300 MHz, preferably standing at 13.56 MHz (authorized frequency with a tolerance of 0.05%) or at 27.12 MHz (authorized frequency with a tolerance of 0.6%).

The generators are outfitted with a safety feature that allows the incident waves to pass through and that diverts the reflected waves to a water load in which the waves are absorbed.

These generators also require the use of iris, of a shortcircuit piston in order to decrease the reflected power and to promote absorption of the generator-transmitted power by the reaction mixture.

The system is outfitted with cooling systems in order to avoid any overheating.

The Buffer Reactors

The buffer reactors permit treating a larger amount of reaction mixture.

The Tanks

The system is outfitted with one or several feeder tank(s), receiver tank(s), filtration tank(s).

The Gas Circuits

The heat treatments are carried out under a normal atmosphere, or an oxygen-rich atmosphere or, preferably, an inert atmosphere.

The Measuring Devices

The system is outfitted with measuring devices such as manometers, thermocouples, flowmeters.

This process can be used in dynamics or in continuum .

- Principle of Intermittent Heating

The entire reaction volume is not continuously exposed to the waves; however, all molecules of the reaction mixture are intermittently subjected to the field.

Various configurations may be considered for carrying out an intermittent dielectric heating.

The first configuration consists in subjecting several reactors to the electromagnetic waves. See Figure N° 1.

The second configuration consists in using several energy applicators on a single reactor. See Figure N° 2.

The number of applicators depends on the desired working temperature, on the amount of product to be treated, on the reaction temperature rise time, on the dielectric constants of the reagents.

Any person skilled in the art will understand that other configurations are possible besides these two and that the invention relates to all other intermediate positions.

Furthermore, the applicant has discovered an original system consisting in circulating the reaction mixture in a loop, thus reducing investment costs for an equivalent production capacity. Without this recycling system, it would indeed be necessary to use a large-size reactor and a multitude of applicators in order to succeed in heating the same amount of products and to achieve the desired result, which would entail enormous costs.

See Figure N° 3.

The intermittent dielectric heating combined with a recycling system makes it possible to increase the production capacities, which are limited under the continuous dielectric

heating system, represented in Figure N° 4 or Figure N° 3 if the applicators cover the entire volume to be treated.

This process can be used in dynamics or in continuum .

According to this configuration, the entire reaction volume is not continuously exposed to the waves; however, all molecules of the reaction mixture are intermittently subjected to the field.

It should be noted that, according to this principle, the invention logically should not have functioned, that is to say, it should logically not have yielded any good results. As a matter of fact, a molecule will only be subjected to the electromagnetic waves for a fraction of its circulation time, for example, 1 sec every 10 sec. Any person skilled in the art understands that this should have produced either very poor results (inefficient process) or zero results. Yet, surprisingly we obtain on the contrary very good results (see hereinbelow) accompanied by the major advantages also mentioned herein.

- Volume Exposed to the Electromagnetic Field

The volume exposed to the electromagnetic field is calculated according to the formula below:

$$V \text{ (exposed to the field)} = \pi * R^2 * H$$

wherein:

R = radius of reactor exposed to the field

H = height of reactor exposed to the field

Parameter H:

The height of the reactor exposed to the field typically corresponds to that of the waveguide in order to permit treating the maximum amount of material all at once.

Let's take the case of heat treatments under singlemode microwave, at 2450 MHz. The height of the waveguide in Mode TE 0.1 (Transverse Electric) is equal to 45mm. The fundamental mode of excitation TE 0.1 makes it possible for the wave to propagate as a single arch, contrary to Mode TE 0.2 which presents two field maxima, yielding a less homogenous heating.

Let's take the case of heat treatments under singlemode microwave, at 915 Hz. In that case, the height of the waveguide is equal to 124 mm.

Parameter R

Typically, the reactor is cylindrical in shape. Its diameter may not exceed the width of the waveguide.

In the case of singlemode microwave applicators, under 2450 MHz, the recommended waveguide width in order to remain in Mode TE 0.1 (Transverse Electric) ranges from about 70 to 100 mm, standing more specifically at 90 mm.

In the case of the singlemode microwave applicators, under 915 MHz, the recommended waveguide width in order to remain in Mode TE 0.1 (Transverse Electric) stands at about 250mm.

- Advantages of the intermittent dielectric heating

Contrary to the common dielectric systems this invention surprisingly permits heating volumes of materials on an industrial scale while keeping the process low-cost. Therefore, the Applicant has devised a process involving intermittent dielectric heating combined with a recycling system.

The Applicant demonstrates, by this invention that the reagents benefit from the advantages inherent to the electromagnetic wave technology without being continuously exposed to the field. Indeed, the benefits of the dielectric heating are preserved:

1. the reaction time is significantly reduced;
2. the reaction is carried out in a single step
3. non-use of solvent

4. energy savings (because the times are significantly shorter)
5. absence of burn-up and side reactions.

Reagents:

For this invention, the reagent(s) can be selected from among the products that are hardly absorbent of electromagnetic waves or the products that are highly absorbent of said electromagnetic waves, or a mixture of both, which may or may not be enhanced by one or several hardly or highly absorbent catalysts or additives and/or process gases.

- vegetable oils

As vegetable oils, we may mention, among others, rapeseed oil, sunflower oil, peanut oil, olive oil, walnut oil, corn oil, soy oil, linseed oil, safflower oil, apricot kernel oil, sweet almond oil, hemp oil, grapeseed oil, copra oil, palm oil, cottonseed oil, Babassu oil, jojoba oil, sesame oil, argan oil, milk-thistle oil, gourdseed oil, raspberry oil, Karanja oil, neem oil, poppyseed oil, Brazilnut oil, castor oil, dehydrated castor oil, hazelnut oil, wheat germ oil, borage oil, oenothera oil, Tung oil, or tall oil.

- animal fats or oils

As animal oils or fats, we can cite, among others, sperm-whale oil, dolphin oil, whale oil, seal oil, sardine oil, herring oil, shark (dog-fish) oil, cod liver oil, neatsfoot oil, as well as beef, pork, horse, mutton tallow (marrow).

- animal or vegetable oil compounds

We can also use compounds of animal or vegetable oils such as squalene extracted from non-saponifiable fats of vegetable oils (olive oil, peanut oil, rapeseed oil, corn germ oil, cottonseed oil, linseed oil, wheat germ oil, rice bran oil) or squalene contained in massive amounts in shark (dog-fish) oil.

These animal or vegetable fats and oils, as well as their derivatives, can undergo a prior treatment intended to make them on the one hand more reactive or on the other hand less reactive. The invention relates to both an isolated reagent and a reaction mixture comprising two or more components. These reaction mixtures can include equivalent proportions of each compound; or, certain compounds can be the primary compounds.

- hydrocarbons

As unsaturated hydrocarbons, we can cite, alone or in a mixture, and as non-limitative examples, an alcene, for example one or several terpenic hydrocarbons, that is to say, one or several polymers of isoprene, or one or several polymers of isobutene, of styrene, of ethylene, of butadiene, of isoprene, of propene, or one or several copolymers of these alkenes.

As saturated hydrocarbons, we can cite, among others, the alkanes, for example ethane, propane.

- saturated and/or unsaturated esters

As for esters of saturated and/or unsaturated fatty acids, we can use such acids either alone or as a mixture, and by way of non-limitative examples, one or several esters obtained by esterification between a monoalcohol and/or polyol and at least one saturated and/or unsaturated fatty acid; waxes; butters, phospholipids; spingolipids; glucolipids.

- saturated and/or unsaturated acids

As unsaturated fatty acids, we can use, either alone or in a mixture, and as non-limitative examples, one or several saturated acids such as caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, one or several monounsaturated fatty acids such as oleic acid, palmitoleic acid, myristic acid, petroselinic acid, erucic acid; one or several polyunsaturated fatty acids such as for example linoleic acid, alpha and gamma linolenic acids, arachidonic acid; 5c,8c,11c,14c-eicosapentaenoic acid (EPA), 4c,7c,10c,13c,16c,19c-docosahexaenoic acid (DHA), one or several acids comprising conjugated dienes or conjugated trienes such as licanic acid, isomers of linoleic and linolenic acids; one or several acids comprising one or several hydroxyl groups such as ricinoleic acid.

- alcohols

As alcohols, we can mention, among others, glycerol, sorbitol, sucrose, mannitol, xylitol, neopentylglycol, pentaerythritol, saccharose, galactose, glucose, maltose, maltotriose, fructose, maltitol, lactitol, lactose, ribose, mellibiose, cellobiose, gentiobiose, altrose, gulose, polyalkyleneglycols, polyglycerols, polyphenols, alkylpolyglucosides, polyglucosides, glycol, pentaerythritol, 1,2-ethanediol, 1,4-butanediol; 1,6-hexanediol, aminoalcohols (for example, diethanol amine (DEA), triethanol amine (TEA), 3-amino-1,2-propanediol), epoxyalcohols, saturated or unsaturated fatty alcohols (for example, myristyl alcohol, oleyl alcohol, lauryl alcohol), linear or branched alcohols, vitamins (for example, tocopherol, ascorbic acid, retinol), sterols (including phytosterols), hemiacetals (for example, 1-ethoxy-1-ethanol), aminoalcohols (for example, 2-2'-aminoethoxy ethanol), epoxyalcohols (for example, 2-3-epoxy-1-propanol), propanol, ethanol, methanol, tetradecyl alcohol and their analogs.

The alcohols as well as their derivatives can undergo a prior treatment intended to make them more reactive or, on the contrary, less reactive, such as for example: hydrogenation, hydroxylation, epoxydation, phosphitation, sulfonation.

- epoxides

As epoxydes, we can use, alone or in a mixture, and as non-limitative examples, vernolic acid, coronaric acid; 1,2-epoxy-9-decene, 3-4-epoxy-1-butene, 2-3-epoxy-1-propanol, fatty esters obtained by esterification between 2-3-epoxy-1-propanol and a fatty acid (for example, Cardura E10®).

- amino alcohols

As amino alcohols, we can use, alone or in a mixture, and as non-limitative examples, monoethanol amine (MEA), diethanol amine (DEA), triethanol amine (TEA), 3-amino- 1,2-propanediol, 1-amino-2-propanol; 2-2'-aminoethoxy ethanol.

- amines

As amines, we can mention, among others, ammonia, primary, secondary and tertiary alkyl amines (for example, methyl amine, dimethyl amine, trimethyl amine, diethyl amine), fatty amines (for example, oleic amines, coconut alkyl amines), amino alcohols (for example, monoethanol amine (MEA), diethanol amine (DEA), triethanol amine (TEA), 3-amino-1,2-propanediol, 1-amino-2-propanol), ethoxylated amines (2-2'-aminoethoxy ethanol, amino-1-methoxy-3-propane).

All these amines can be saturated or nonsaturated, linear or branched.

- catalysts

Among the catalysts or additives, there shall be, as non-limitative examples, the common acid catalysts (para toluene sulfonic acid, sulfuric acid, phosphoric acid, perchloric acid, etc.), the common basic catalysts (soda, potash, alcoholate of alkaline metals and of

alkaline-earth metals, sodium acetate, triethyl amines, pyridine derivatives, etc.), acid and/or basic resins of the Amberlite™, Amberlyst™, Purolite™, Dowex™, Lewatit™ types, zeolithes and enzymes, carbon blacks, and activated carbon fibers.

The invention will be better understood upon reading the following description and the non-limitative examples given below.

EXAMPLES

The examples given below highlight the value of the invention and will allow any person skilled in the art to easily extrapolate to other dimensions and/or geometries without departing from the true scope and spirits of the invention in its broader aspects.

Additionally, the following examples, which are given solely for purposes of description and in no way of limitation, illustrate the value of the invention. These examples aim to demonstrate that the intermittent dielectric heating process is low-in-cost and permits heating reaction volumes on an industrial scale while still benefiting from the advantages of this technology.

I. Volumes Exposed to Electromagnetic Waves

The tests were conducted on the laboratory and on industrial scale using two (2) generators:

- one (1) 6kW magnetron generator operating at the 2450 MHz frequency for the laboratory treatments
- one (1) 60 kW magnetron generator operating at the 915 MHz frequency for the industrial treatments

	D (mm)	H (mm)	Unit Vexp	Number of reactors	Total Vexp
Pilot	30	45	32 mL	1	32 mL
Industrial	100	124	1 L	4	4 L

wherein:

D = diameter of cylindrical reactors = 2R

H = height of waveguide

Unit V_{exp} = volume exposed continually basis to waves for one reactor

Total V_{exp} = volume exposed continually to waves for both reactors

$$V (\text{exposed to the field}) = \pi * R^2 * H$$

II. Comparison between Conventional Heating and Intermittent Dielectric Heating

a. Polyglycerol synthesis

The tests are conducted at 260°C, in the presence of 2% sodium acetate in order to obtain a polyglycerol with a viscosity at 50°C equal to 3600cP.

They make reference to Patent Application FR N° 0108906.

		Total V of glycerol	V ratio	Reaction Time
Intermittent dielectric heating	Pilot	2,000 mL	1/62	3 h
	industrial	200 L	1/50	6 h 30 min
Conventional heating	Schou			> 72 h

wherein:

Total V of glycerol = total volume of glycerol treated

V ratio = ratio between the volume exposed to waves and the total volume treated

b. Synthesis of polyglycerol esters

Synthesis of polyglycerol-6 dioleate

The tests are carried out in the presence of 0.25% sodium acetate at 230°C.

They make reference to Patent Application FR N° 0108906.

	Total V of mixture	V ratio	Reaction time
Intermittent dielectric heating	2000 mL	1/62	2 h 10 min
Conventional heating			4 h 30 min

wherein:

Total V of mixture = total volume treated

V ratio = ratio between the volume exposed to waves and the total volume treated

Synthesis of polyglycerol-2 tristearate

The tests are carried out in the presence of 0.25% sodium acetate at 260°C.

They make reference to Patent Application FR N° 0108906.

	Total V of mixture	V ratio	Reaction time
Intermittent dielectric heating	2000 mL	1/62	1 h 40 min
Conventional heating			4 to 5 h

wherein:

Total V of mixture = total volume treated

V Ratio = ratio between the volume exposed to waves and the total volume treated

c. Conclusion

Even if the entire reaction volume is not exposed to electromagnetic waves, the reaction times under intermittent dielectric heating are considerably lower than those obtained with conventional heating.

III. Comparison between intermittent dielectric heating and continuous dielectric heating

a. Efficiency of intermittent dielectric heating

The table below shows the efficiency of intermittent dielectric heating compared with continuous dielectric heating which is typically used.

The tests are carried out under the same conditions (composition of reaction mixtures, temperatures, catalysts, etc.)

- at the laboratory scale (use of a Synthewave 402) which uses continuous dielectric heating
- at the pilot scale, using a 2450 MHz generator that uses intermittent dielectric heating
- and at the production scale using a 915 MHz generator that uses intermittent dielectric heating

The synthesis tested consists in manufacturing unsaturated fatty acid polymers, unsaturated fatty acid esters, unsaturated hydrocarbons, unsaturated derivatives of these compounds, alone or in a mixture.

Laboratory	Pilot	Industrial
------------	-------	------------

	Mop	MOi	Extrapolated Mop	MOi	Extrapolated Mop
V _{treated} (mL)	25	2000	2000	200000	200000
V ratio	1/1	1/62	1/1	1/50	1/1
t _{reaction} (h)	2h15min	2h15min	≥ 2h15**	2h15	≥ 2h15**

wherein:

Mop = continuous microwave heating

Extrapolated Mop = continuous microwave heating in the case of treatment of 200kg of product

MOi = intermittent microwave heating

V_{treated} = reaction volume treated

V ratio = ratio between the volume exposed to electromagnetic waves and the total reaction volume

t_{reaction} = reaction time

** : Treating a large amount of products requires a reaction time greater than or equal to that for a lower amount. The reaction time is 2h15 for 25mL of product. Thus, it can be asserted that the reaction time needed to treat 200kg of the same mixture will be greater than or equal to 2h15.

This table shows that the reaction times are unchanged, whether one works on 25 mL, 2 kg, or 200 kg. However, in the case of pilot and industrial tests (2 kg and 200 kg), the entire volume is not subjected to dielectric heating:

- laboratory test (continuous dielectric heating): the entire volume is exposed to electromagnetic waves with Ratio = 1/1

- pilot test (intermittent dielectric heating): only 1/62 of the volume is exposed to the field
- industrial test (intermittent dielectric heating): only 1/50 of the volume is exposed to the field

b. Lowering of Investment Costs

If we had to treat 200 liters of product using continuous dielectric heating, we would have to expose all 200 liters to the electromagnetic waves.

By working at the 2450 MHz frequency, the maximum volume exposed by applicator is 32 mL. Here this configuration is not advantageous at all. In fact, we would need 6250 applicators.

By working at the 915 MHz frequency, the maximum volume exposed by applicator is 1L. We would then need 200 applicators.

For this invention, intermittent dielectric heating makes it possible to use only four (4) applicators, that is to say, 50 times less (a ratio consistent with that given in the preceding table) for the same production capacity.

We can compare the investment costs:

X = investment cost of a system with intermittent dielectric heating, 4 channels, recycling

Y = investment cost of a system with continuous dielectric heating, 200 channels, without recycling

$$Y = 10 \cdot X$$

The investment cost would then be 10 times higher in the case of a continuous dielectric heating compared with intermittent dielectric heating. This is essentially due to the cost of applicators, which is much higher than the rest of the system (buffer reactor, recycling pump, etc.).

CLAIMS

1. A heat treatment process in a chemical synthesis, of the dielectric type, characterized in that said dielectric heating is carried out intermittently, that is to say, the reagent or reagents is/are subjected to electromagnetic waves intermittently, in combination with a recycling system.
2. A process as claimed in Claim 1 wherein the electromagnetic waves are selected in the frequencies ranging between 300 GHz and 3 MHz.
3. A process as claimed in Claim 2 wherein the frequencies are selected from among:
 - *MW frequencies and HF*
 - Those microwave frequencies (MW) that range from about 300 MHz to about 30 GHz, preferably standing at 915 MHz (authorized frequency with a tolerance of 1.4%) or at 2.45 GHz (authorized frequency with a tolerance of 2%).
 - Those high frequencies (HF) that range from about 3 MHz to about 300 MHz, preferably standing at 13.56 MHz (authorized frequency with a tolerance of 0.05%) or at 27.12 MHz (authorized frequency with a tolerance of 0.6%).
4. A process as claimed in any of Claims 1 to 3, wherein the entire reaction volume is not continuously exposed to dielectric waves but wherein all reaction mixture molecules are intermittently subjected to the field.
5. A process as claimed in any of Claims 1 to 4, wherein the reagent(s) can be selected from among those products that hardly absorb the electromagnetic waves or those products that are highly absorbent of said waves or a mixture of both, whether or not

enhanced with one or several hardly or highly absorbent catalysts or additives and/or process gas.

6. A process as claimed in Claim 5 wherein the reagent(s) is/are selected from among:

- *vegetable oils*

rapeseed oil, sunflower oil, peanut oil, olive oil, walnut oil, corn oil, soy oil, linseed oil, safflower oil, apricot kernel oil, sweet almond oil, hemp oil, grassed oil, copra oil, palm oil, cottonseed oil, Babes oil, jujube oil, sesame oil, argon oil, milk-thistle oil, gourds oil, raspberry oil, Carnage oil, enema oil, poppies oil, Brazilnut oil, castor oil, dehydrated castor oil, hazelnut oil, wheat germ oil, borage oil, oenothera, oil, Tung oil, or tall oil.

- *animal fats or oils*

sperm-whale oil, dolphin oil, whale oil, seal oil, sardine oil, herring oil, shark (dog-fish) oil, cod-liver oil, neatsfoot oil, as well as beef, pork, horse, mutton tallow (marrow).

- *compounds of animal or vegetable oils*

squalene extracted from non-saponifiable fats of vegetable oils (olive oil, peanut oil, rapeseed oil, corn germ oil, cottonseed oil, linseed oil, wheat germ oil, rice bran oil) or squalene contained in large amounts in shark (dog-fish) oil.

- *hydrocarbons*

unsaturated: alone or in a mixture, an alcene, for example one or several terpenic hydrocarbons, that is to say, one or several polymers of isoprene, or one or several polymers of isobutene, of styrene, of ethylene, of butadiene, of isoprene, of propene, or one or several copolymers of these alkenes.

saturated: alkanes, for example ethane, propane.

- saturated and/or unsaturated esters

alone or in a mixture, one or several esters obtained by esterification between a monoalcohol and/or polyol and at least one saturated and/or unsaturated fatty acid; waxes; butters, phospholipids; spingolipids; glucolipids.

- saturated and/or unsaturated acids

alone or in a mixture, one or several saturated acids such as caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, one or several monounsaturated fatty acids such as oleic acid, palmitoleic acid, myristic acid, petroselenic acid, erucic acid; one or several polyunsaturated fatty acids such as for example linoleic acid, alpha and gamma linolenic acids, arachidonic acid; 5c,8c,11c,14c-eicosapentaenoic acid (EPA), 4c,7c,10c,13c,16c,19c-docosahexaenoic acid (DHA), one or several acids comprising conjugated dienes or conjugated trienes such as licanic acid, isomers of linoleic and linolenic acids; one or several acids comprising one or several hydroxyl groups such as ricinoleic acid.

- *alcohols*

glycerol, sorbitol, sucrose, mannitol, xylitol, neopentylglycol, pentaerythritol, saccharose, galactose, glucose, maltose, maltotriose, fructose, maltitol, lactitol, lactose, ribose, mellibiose, cellobiose, gentiobiose, altrose, gulose, polyalkyleneglycols, polyglycerols, polyphenols, alkylpolyglucosides, polyglucosides, glycol, pentaerythritol, 1,2-ethanediol, 1,4-butanediol; 1,6-hexanediol, aminoalcohols (for example, diethanol amine (DEA), triethanol amine (TEA), 3-amino-1,2-propanediol), epoxyalcohols, saturated or unsaturated fatty alcohols (for example, myristyl alcohol, oleyl alcohol, lauryl alcohol),

linear or branched alcohols, vitamins (for example, tocopherol, ascorbic acid, retinol), sterols (including phytosterols), hemiacetals (for example, 1-ethoxy-1-ethanol), aminoalcohols (for example, 2-2'-aminoethoxy ethanol), epoxyalcohols (for example, 2-3-epoxy-1-propanol), propanol, ethanol, methanol, tetradecyl alcohol and their analogs.

- *epoxides*

alone or in a mixture, vernolic acid, coronaric acid, 1,2-epoxy-9-decene, 3-4-epoxy-1-butene, 2-3-epoxy-1-propanol, fatty esters obtained by esterification between 2-3-epoxy-1-propanol and a fatty acid (for example, Cardura E10®).

- *amino alcohols*

alone or in a mixture, monoethanol amine (MEA), diethanol amine (DEA), triethanol amine (TEA), 3-amino-1,2-propanediol, 1-amino-2-propanol; 2-2'-aminoethoxy ethanol.

- *amines*

ammonia, primary, secondary and tertiary alkyl amines (for example, methyl amine, dimethyl amine, trimethyl amine, diethyl amine), fatty amines (for example, oleic amines, coconut alkyl amines), amino alcohols (for example, monoethanol amine (MEA), diethanol amine (DEA), triethanol amine (TEA), 3-amino-1,2-propanediol, 1-amino-2-propanol), ethoxylated amines (2-2'-aminoethoxy ethanol, amino-1-methoxy-3-propane), which amines can be saturated or unsaturated, linear or branched.

7. A process as claimed in Claim 6, wherein the animal or vegetable fats and oils, as well as their derivatives, can undergo a prior treatment intended to make them on the one hand more reactive or on the other hand less reactive (both an isolated reagent and a reaction mixture comprising two or several compounds, which reaction mixtures can

comprise equivalent proportions of each compound, or some compounds can be majority compounds).

8. A process as claimed in Claim 6 or 7, wherein the alcohols as well as their derivatives can undergo a prior treatment intended to make them on the one hand more reactive or on the other hand less reactive, such as for example hydrogenation, hydroxylation, epoxidation, phosphitation, sulfonation.

9. A process as claimed in any of Claims 1 to 8, wherein it uses as catalysts or additives:

- catalysts

the common acid catalysts (para toluene sulfonic acid, sulfuric acid, phosphoric acid, perchloric acid, etc.), the common basic catalysts (soda, potash, alcoholate of alkaline metals and of alkaline-earth metals, sodium acetate, triethyl amines, pyridine derivatives, etc.), acid and/or basic resins of the Amberlite™, Amberlyst™, Purolite™, Dowex™, Lewatit™ types, zeolithes and enzymes, carbon blacks, and activated carbon fibers.

10. A process as claimed in any of Claims 1 to 9, wherein the volume exposed to electromagnetic waves is with:

- one (1) 6kW magnetron generator operating at the 24500 MHz frequency for the laboratory treatments
- one (1) 60kW magnetron generator operating at the 915 MHz frequency for the industrial treatments

	D (mm)	H (mm)	Unit Vexp	Number of reactors	Total Vexp
Pilot	30	45	32 mL	1	32 mL
Industrial	100	124	1 L	4	4 L

wherein:

D = diameter of cylindrical reactors = 2R

H = height of waveguide

Unit Vexp = volume exposed to waves on a continuous basis for one reactor

Total Vexp = volume exposed to waves on a continuous basis for both reactors

$$V \text{ (exposed to the field)} = \Pi * R^2 * H$$

11. A device for the implementation of the process as claimed in any of Claims 1 to 10, wherein it comprises or consists of :

A)

- pumps
- reactors subjected to the electromagnetic field
- a dielectric system: chimney applicators, generator waveguides, iris, short-circuit piston, cooling systems
- buffer reactors
- tanks
- a gas circuit, preferably for an inert gas such as nitrogen
- condensers
- measuring devices

-and in particular B)

- pumps

The pump(s) is/are of the variable flow type.

It can be a feeder dosing pump and/or a recycling pump and/or a vacuum pump. The outflow of the recycling pump influences the time required for a molecule to transit under the waves.

The pumps can be selected, for purpose of indication, from among vane pumps or piston pumps.

- one or several reactors subjected to electromagnetic waves
 - a) The reactors subjected to the electromagnetic field do not absorb waves (pyrex, quartz, etc.).
 - b) They are typically cylindrical in shape.
 - c) They are positioned inside the applicators.
- a dielectric system: energy applicators, chimneys, waveguides, generator, iris, and short-circuit piston, cooling systems.

- a) The applicators are formed by singlemode cavities that resonate at the transmission frequency according to a radiation in the direction of the waveguide.
- b) The chimneys prevent wave leakage to the outside of the waveguide. They are preferably of a conical cylindrical shape, as indicated in Application FR N° 0108906 filed by this Applicant for limiting the presence of electric arcs.
- c) The waveguide(s) carries/carry the electromagnetic waves. Each waveguide can be subdivided into two — and only two — waveguides.
- d) The generators used are microwave or high-frequency generators.
- e) The microwave (MW) frequencies range from about 300 MHz to about 30 GHz, preferably standing at 915 MHz (authorized frequency with a tolerance of 1.4%) or at 2.45 GHz (authorized frequency with a tolerance of 2%).
- f) The high frequencies (HF) range from about 3 MHz to about 300 MHz, preferably standing at 13.56 MHz (authorized frequency with a tolerance of 0.05%) or at 27.12 MHz (authorized frequency with a tolerance of 0.6%).
- g) The generators are outfitted with a safety feature that allows the incident waves to pass through and that diverts the reflected waves to a water load in which the waves are absorbed.
- h) These generators also require the use of iris, of a shortcircuit piston in order to decrease the reflected power and to promote absorption of the generator-transmitted power by the reaction mixture.
- i) The system is outfitted with cooling systems in order to avoid any overheating.

- buffer reactors

The buffer reactors permit treating a larger amount of reaction mixture.

- tanks

The system is outfitted with one or several feeder tank(s), receiver tank(s), filtration tank(s).

- gas circuits

The heat treatments are carried out under a normal atmosphere, or an oxygen-rich atmosphere or, preferably, an inert atmosphere.

- measuring devices

The system is outfitted with measuring devices such as manometers, thermocouples, flowmeters.

12. A device as claimed in Claim 11, wherein the process can be used in dynamics or in continuum.

13. A device as claimed in Claims 11 or 12, wherein it uses as energy applicator:

- *type of energy applicators*

— As regards high frequency applicators, they consist mainly in:

- applicators of the capacitive type formed by two condenser armatures between which the generator's high-frequency voltage is applied. They are used for the

heat treatment of materials whose volume constitutes a parallelepiped, one side of which is sufficiently thick (>10 mm).

- applicators with rods for planar materials. These applicators are made up of tubular or rod-shaped electrodes. They are used for the heat treatment of materials whose volume constitutes a parallelepiped, one side of which is insufficiently thick (<10 mm).

- applicators for filiform materials, formed by loops.

— As regards microwave applicators, we can cite:

- the localized-field applicators: singlemode cavity
- the diffuse-field applicators: multimode cavity
- the near-field applicators: {wave}guide with radiating antennas

14. A device as claimed in any of Claims 11 to 13, wherein :

- The "singlemode" system (localized field) which is formed by singlemode cavities resonating at the transmission frequency according to a radiation in the direction of the {wave}guide, is preferable to the "multimode" (diffuse field).
- The applicator is outfitted with regular cylindrical chimneys.
- The device includes good venting with humid air or with some other comparable gas as regards its dielectric constants (for example, sulfur hexafluoride SF₆ under 1 bar) or chimneys with specially adapted shapes so as to eliminate static electricity formed on the outside wall of the reactor.

15. A device as claimed in any of Claims 11 to 14, wherein a specific chimney geometry is used, in particular a conical chimney.

16. A device as claimed in any of Claims 11 to 15, wherein the reactor is typically cylindrical in shape, and its diameter may not exceed the width of the waveguide.

17. A device as claimed in any of Claims 11 to 16, wherein in the case of singlemode microwave applicators, under 2450 MHz, the waveguide width recommended in order to remain in the TE 0.1 (Transverse Electric) mode stands between about 70 and 100 mm, and more specifically at 90 mm.

18. A device as claimed in any of Claims 11 to 16, wherein in the case of singlemode microwave applicators, under 915 MHz, the waveguide width recommended to remain in the TE 0.1 (Transverse Electric) mode is about 250 mm.

19. A device as claimed in any of Claims 11 to 18, wherein the dielectric system comprises applicators, chimneys, waveguides, a generator, iris, a shortcircuit piston, cooling systems, as follows:

- The applicators are formed by singlemode cavities that resonate at the transmission frequency according to a radiation in the direction of the waveguide.

- The chimneys prevent wave leakage to the outside of the waveguide. They are preferably of a conical cylindrical shape, as indicated in Patent Application FR N°0108906 filed by this Applicant for limiting the presence of electric arcs.

- The waveguide(s) carries/carry the electromagnetic waves. Each waveguide can be subdivided into two — and only two — waveguides.

- The device also uses iris, short-circuit piston in order to lower the reflected power and to promote absorption of the generated-transmitted power by the reaction mixture.

20. A Process and Device as claimed in any of Claims 1 to 19, characterized in that the heat treatments are carried out under a normal atmosphere, or an oxygen-rich atmosphere, or preferably under an inert atmosphere.

21. Applications of the process as claimed in any of Claims 1 to 10 and 20 and of the device as claimed in any of Claims 11 to 19 in all "heat applications", that is to say, those chemical syntheses involving a heat treatment and the use of a single reagent, or a mixture of reagents, in variable proportions, with or without catalysts, with or without process gas.

22. Applications as claimed in Claim 21, wherein as "heat applications" we can cite, as non-limitative examples, such reactions as esterification, transesterification, epoxidation, sulfatation, phosphitation, hydrogenation, peroxidation, isomerization, dehydration, quaternization, amidation, polymerization, polycondensation, and all the common treatments such as decolorizing, deodorizing, and the other systems for eliminating volatile compounds.

23. Applications of the process as claimed by any of Claims 1 to 10 and 21 and of the device as claimed by any of Claims 11 to 19 to all "lipochemistry" reactions.

24. Applications of the process as claimed in any of claims 1 to 10 and 21 and of the device as claimed in any of Claims 11 to 19 for manufacturing polymers of unsaturated fatty acids, of unsaturated fatty acid esters, of unsaturated hydrocarbons or of derivatives of these products using intermittent dielectric heating under microwaves.

25. Applications of the process as claimed in any of Claims 1 to 10 and 21 and of the device as claimed in any of Claims 11 to 19 specific to the synthesis of:

- polyglycerol
- polyglycerol esters
- polyglycerol-6 dioleate
- polyglycerol-2 tristearate

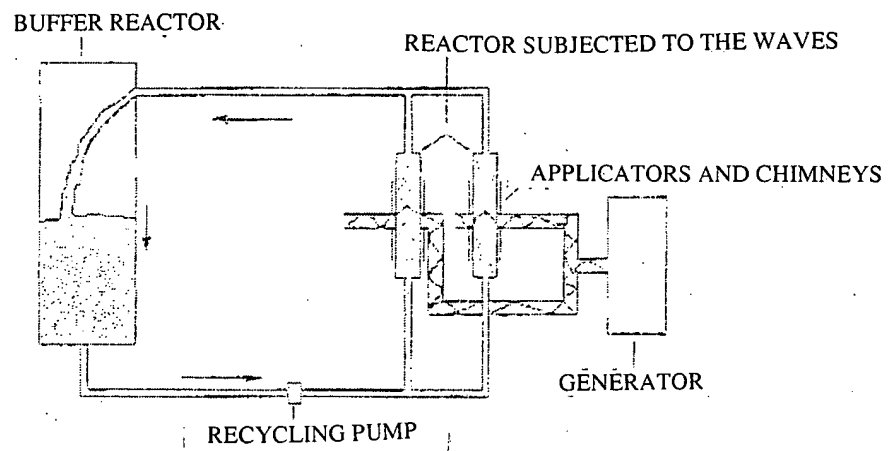


Figure 1

2/4

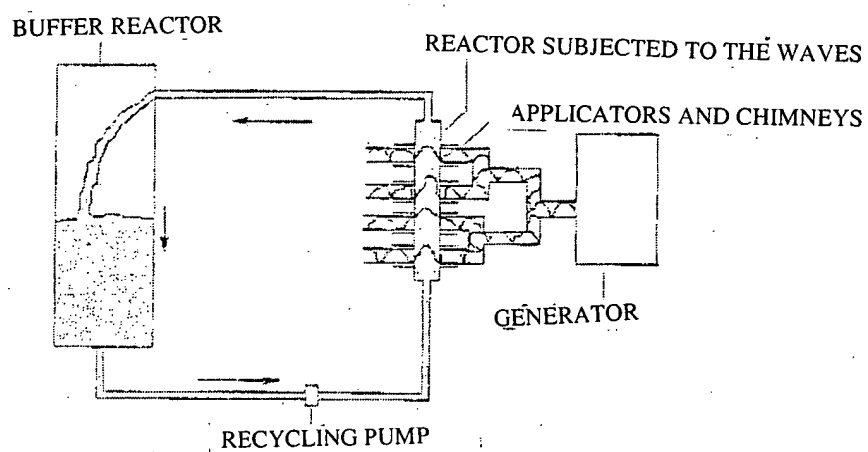


Figure 2

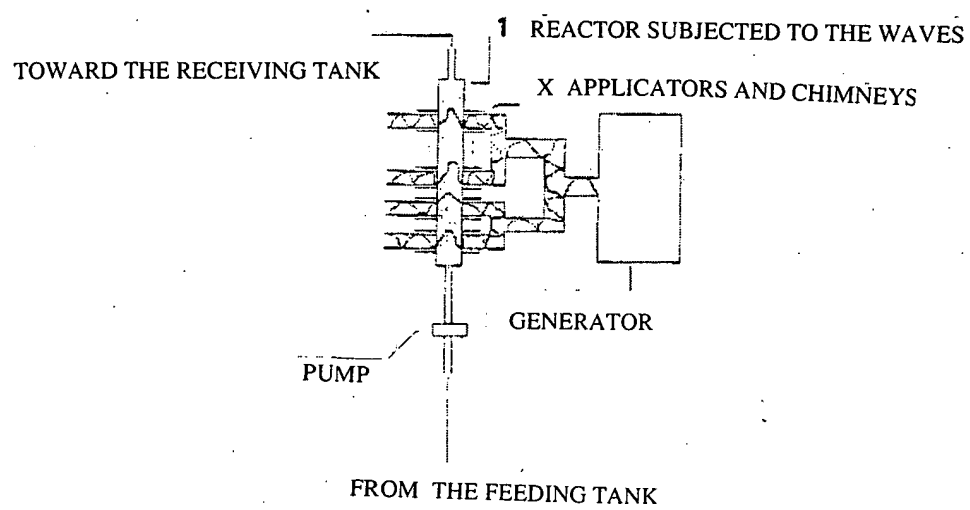


Figure 3

4 / 4

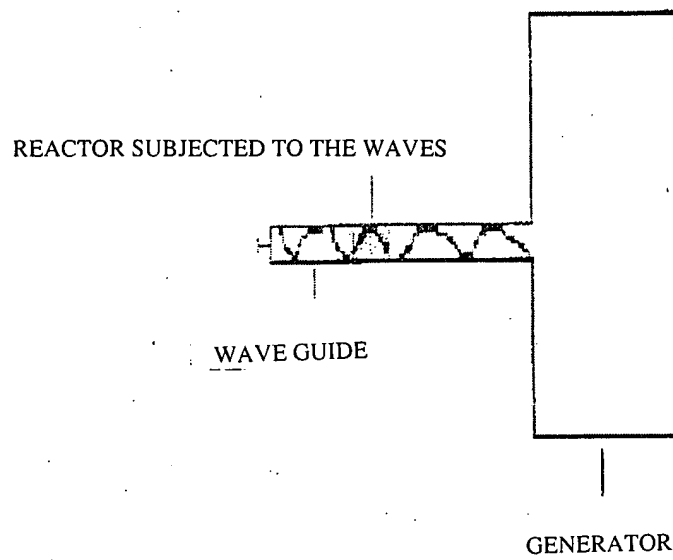


Figure 4